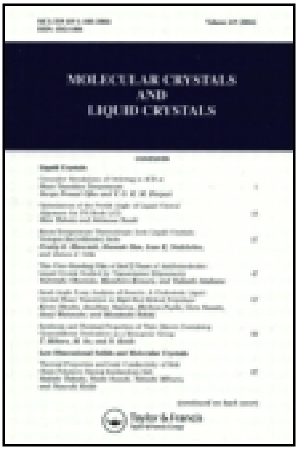

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Numerical Prediction of Twisting Power for Chiral Dopants

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NUMERICAL PREDICTION OF TWISTING POWER FOR CHIRAL DOPANTS

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Abstract We have implemented a theoretical model for the numerical evaluation of the helical twisting power of chiral dopants in liquid crystal phases, on the basis of their shape and of solvent macroscopic properties. After summarizing the fundamentals of the method, the numerical procedure is briefly illustrated and the application to the case of biphenyl derivatives is presented.

INTRODUCTION

The addition of traces of chiral solutes to nematic liquid crystal phases induces the formation of "twisted nematic" structures, traditionally termed cholesterics [1]. The helical superstructures obtained in this way are characterized by their handedness and pitch, and they are of relevant interest in the field of optical devices.

Recently, a theoretical model was derived [2–4], which is able to predict handedness and pitch of the chiral phase starting from a description of the shape of the chiral dopant. Besides a few prototype systems, the model was tested successfully on a series of heptalene derivatives, for which experimental data were available [5]. In the present paper, we shall extend our analysis to a series of biphenyl derivatives which are kept in specific structural forms by suitable substituents hindering internal rotations [6,7]. These systems represent a crucial test, because of the presence of the complex substituents and of a certain degree of internal flexibility. It will be shown that also for this series satisfactory agreement between model predictions and experimental results is obtained.

ORIENTING POTENTIAL AND TWISTING POWER

A molecule embedded in a locally uniaxial liquid crystal environment is assumed to experience an orienting potential which tends to align each element dS of its surface with the mesophase director, according to the expression [2–4]:

$$U(\Omega)/k_BT = \varepsilon \int P_2(\underline{n} \cdot \underline{s})\, dS, \tag{1}$$

where ε is the orienting strength of the medium, Ω are the Euler angles for the transformation from a molecular to a laboratory frame, P_2 is the second Legendre polynomial, $\underline{n}$ is a unit vector parallel to the local director and $\underline{s}$ is a unit vector along the outer normal to the surface element dS. By use of the addition theorem for spherical harmonics, eq. (1) is conveniently rewritten in terms of molecular tensors and angular functions relating laboratory and molecular frames. In cholesteric phases the director rotates so as to produce a helical macrostructure, which is characterized by its handedness and pitch p, or by the wave vector $\underline{q}$ of magnitude $q = 2\pi/p$. Since typical values of helical pitches, which are of the order of micrometers, are much larger than the molecular dimensions, the q-expansion of the orienting potential can be reasonably truncated at the first term. Thus, it can be shown that the orienting potential can be approximated as:

$$U(\Omega)/k_BT = -\varepsilon \sum_m \{T^{(2,m)\,*} - qQ^{(2,m)\,*}\}\mathcal{D}^2_{0m}(\Omega), \tag{2}$$

where $\mathcal{D}^2_{0m}(\Omega)$ are Wigner rotation functions and $T^{(2,m)}$, $Q^{(2,m)}$ are irreducible spherical components of second rank molecular tensors, termed surface and helicity tensor, respectively [2–4]. They are related to morphological properties of the molecule. The surface tensor, whose elements are related to projections of the molecular surface on the planes of the molecular frame, determines the orienting behaviour of the molecule. The helicity tensor is a pseudotensor measuring the helicities as viewed along the molecular axes, and it accounts for the chiral properties of the molecule.

On the basis of this model for the orienting potential, a statistical thermodynamics derivation leads to the following expression for the helical twisting power of a given chiral solute in a nematic solvent, in terms of orientational order parameters and helicity tensor components of the solute, in addition to solvent properties [4]:

$$\beta = RT\varepsilon\mathcal{Q}/2\pi K_{22}v_m. \tag{3}$$

In this equation K_{22} and v_m are twist elastic constant and molar volume of the solvent, and $\mathcal{Q}$ is a chirality order parameter which is defined as:

$$\mathcal{Q} = -\sum_m Q^{(2,m)\,*}\overline{\mathcal{D}^2_{0m}(\Omega)}, \tag{4}$$

where

$$\overline{\mathcal{D}^2_{0m}(\Omega)} = \int \mathcal{D}^2_{0m}(\Omega)\ P(\Omega)\ d\Omega \tag{5}$$

with the orientational distribution function

$$P(\Omega) = \exp[-U(\Omega)/k_BT]/\int \exp[-U(\Omega)/k_BT]\ d\Omega. \tag{6}$$

SURFACE AND HELICITY TENSORS

These tensors have been derived and discussed elsewhere [2-4]. However, in the following we shall stress some points which are of interest to highlight the properties of the tensors and to implement their calculation.

In terms of the vector components in the molecular frame, the orienting potential can be rewritten in the following form:

$$U(\Omega)/k_BT = \varepsilon \sum_{i,j=x,y,z} \int_s \frac{3n_in_js_is_j - \delta_{ij}}{2}\ dS, \tag{7}$$

where the projections of the director on the molecular axes depend on the orientation of the molecule. In a cholesteric phase with pitch p, let us take a laboratory frame with the origin coincident with the origin of the molecular frame, and the axes defined in such a way that the Y axis is parallel to the helical axis while the Z axis is parallel to the director at the origin. The orientation of the director at the position $\underline{r}$ is then defined by the relation:

$$\underline{n} = \underline{e}_Z \cos \underline{q} \cdot \underline{r} + \underline{e}_X \sin \underline{q} \cdot \underline{r}, \tag{8}$$

where $\underline{e}_I$ are unit vectors along the axes of the laboratory frame, and $\underline{q}$ is the wave vector, parallel to the helical axis. By making use of this expression, in the limit $q \to 0$ eq. (7) can be rewritten as:

$$\begin{aligned} U(\Omega)/k_BT =& \varepsilon \left[\sum_{i,j=x,y,z} l_{Zi}l_{Zj} \int_S \frac{3s_is_j - \delta_{ij}}{2}\ dS \right. \\ & \left. + 3q \sum_{i,j,k=x,y,z} l_{Xi}l_{Yj}l_{Zk} \int_S s_ir_js_k\ dS\} \right], \end{aligned} \tag{9}$$

where l_{Ij} is the director cosine between the j-th molecular axis and the laboratory I-th axis. The products s_is_j and $s_ir_js_k$ are components of the second rank tensor $\underline{s} \otimes \underline{s}$ and of the third rank tensor $\underline{s} \otimes \underline{r} \otimes \underline{s}$. The latter can be decomposed as a sum of reducible tensors of rank up to three; if only the second-rank terms are retained, eq. (9) can be approximated as:

$$U(\Omega)/k_BT = -\varepsilon(3/2)\underline{l}_Z \cdot \left[\underline{\underline{t}} - \frac{1}{3}\mathrm{Tr}(\underline{\underline{t}}) - q\,\frac{\underline{\underline{q}}+\underline{\underline{\tilde{q}}}}{2}\right] \cdot \underline{l}_Z, \tag{10}$$

where

$$\underline{\underline{t}} = -\int_S \underline{s} \otimes \underline{s}\; dS, \tag{11}$$

$$\underline{\underline{q}} = -\int_S \underline{r} \times \underline{s} \otimes \underline{s}\; dS, \tag{12}$$

and $\underline{\underline{\tilde{q}}}$ is the transpose of $\underline{\underline{q}}$:

$$\underline{\underline{\tilde{q}}} = \int_S \underline{s} \otimes \underline{s} \times \underline{r}\; dS. \tag{13}$$

It is interesting to observe that $\underline{\underline{t}}$ and $\underline{\underline{q}}$ have the same form as the tensors for the translational and roto-translational hydrodynamic friction [8], respectively. They are only determined by the exterior geometry of the particle. Exactly as the roto-translational coupling tensor, $\underline{\underline{q}}$ is a pseudotensor dependent upon the location of the origin, which obeys the symmetry requirements specific for chiral objects. The transformation law for translation of the origin from O to O' is:

$$\underline{\underline{q}}^{O} = \underline{\underline{q}}^{O'} + \underline{r}^{OO'} \times \underline{\underline{t}} \tag{14}$$

where $\underline{r}^{OO'}$ is the position vector of O' in the molecular frame with the origin in O. In general the tensor $\underline{\underline{q}}$ is not symmetric; it can be decomposed into symmetric and antisymmetric parts:

$$\underline{\underline{q}}_s = (\underline{\underline{q}} + \underline{\underline{\tilde{q}}})/2 \tag{15}$$

$$\underline{\underline{q}}_a = (\underline{\underline{q}} - \underline{\underline{\tilde{q}}})/2 \tag{16}$$

It can be demonstrated that every molecule possesses a unique point at which the antisymmetric contribution vanishes [8]; this point will be denoted as the helicity center H.

It has to be remarked that the tensors $\underline{\underline{t}}$ and $\underline{\underline{q}}$ are not exactly the surface and the helicity tensors appearing in eq. (2) and defined elsewhere

[2–4]. They have been introduced here in order to make apparent the formal analogy with tensors describing the hydrodynamic friction of rigid bodies. Actually, the tensor $\underline{\underline{T}}$ is obtained from $\underline{\underline{t}}$, apart from a numerical factor, after subtracting its trace:

$$\underline{\underline{T}} = \frac{3\underline{\underline{t}} - \mathrm{Tr}(\underline{\underline{t}})}{\sqrt{6}} = \frac{3\underline{\underline{t}} + S\underline{\underline{1}}}{\sqrt{6}}, \tag{17}$$

while the helicity tensor $\underline{\underline{Q}}$ is proportional to the symmetric part of $\underline{\underline{q}}$:

$$\underline{\underline{Q}} = \sqrt{3/8}(\underline{\underline{q}} + \underline{\underline{\tilde{q}}}). \tag{18}$$

COMPUTATIONAL PROCEDURE

Calculation of surface and helicity tensors requires knowledge of the molecular structure which is taken from literature, when available. Otherwise, it can obtained by geometry optimization [see, *e.g.* ref. [9]]. The molecular surface is defined as the outer surface of an assembly of interlocking spheres centered at the atomic positions. The van der Waals radii of atoms or pseudoatoms are taken from the literature [10,11]

The surface tensor is evaluated by partitioning each sphere in a grid of elements, whose contribution is retained only if they belong to the outer surface; thus the surface tensor of a molecule is calculated by summing up contributions deriving from the various spheres:

$$\underline{\underline{t}} = \sum_p \underline{\underline{t}}_p \tag{19}$$

A simple expression for the helicity tensor is obtained by exploiting the property that for a sphere the vector position $\underline{r}$ of a given surface element in a molecular frame with the origin in the centre of the sphere is parallel to the outer normal $\underline{s}$. Therefore, the contribution of the pth sphere to the helicity tensor vanishes, if it is calculated in a molecular frame with the origin at the centre, O_p. Thus, it follows from eq. (14) that the tensor $\underline{\underline{q}}^O$ can be calculated as:

$$\underline{\underline{q}}^O = \sum_p \underline{r}^{OO_p} \times \underline{\underline{t}}_p. \tag{20}$$

The helicity tensor is conveniently expressed in a molecular frame with the origin in the helicity center H. Apart from cases in which it is determined by symmetry, the location of this point is in general unknown. It can be found by using the condition of vanishing values for the antisymmetric components of $\underline{\underline{q}}^{H}$. This leads to a system of three linear equations for the components of the vector $\underline{r}^{OH}$:

$$\left(\underline{r}^{OH} \times \underline{\underline{t}} + \underline{\underline{t}} \times \underline{r}^{OH}\right)_{ij} = \sum_{p} \left(\underline{r}^{OO_p} \times \underline{\underline{t}}_{p} + \underline{\underline{t}}_{p} \times \underline{r}^{OO_p}\right)_{ij}, \qquad (21)$$

where i and j are labels for molecular axes, and $i \neq j$.

Once the tensors $\underline{\underline{t}}$ and $\underline{\underline{q}}$ have been calculated, surface and helicity tensors are obtained according to eqs. (17) and (18). Then, the orientational order parameters $\overline{\mathcal{D}}^{2}_{0m}(\Omega)$ and the chirality order parameter Q can be evaluated on the basis of eqs. (3) and (4). It appears from the definitions that they depend on the value of the parameter ε, which gives the orienting strength of the medium and can be related to the reduced temperature by the Maier-Saupe theory, as shown in ref. [3].

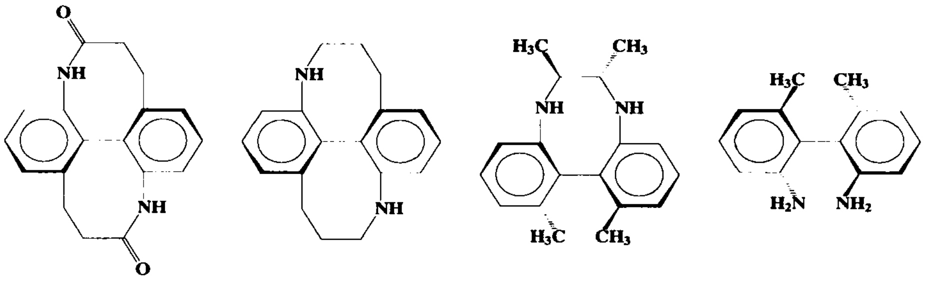
AN EXAMPLE: CHIRAL BIPHENYL DERIVATIVES

We shall discuss in the following the case of four diaminobiphenyls shown in Fig. 1, which in the past have been investigated from the point of view of both their twisting ability [6] and chiroptical properties [7].

It has been shown [6,12] that binaphthyl derivatives with substituents hindering the rotation of the aromatic moieties induce cholesteric phases having their same helicity: that is, M (P) biphenyls induce M (P) cholesterics.

Before commenting on our results, some words about the geometry of the compounds are in order. X-ray structures have been reported in ref. [7] for crystals of (2), (3) and (4). According to such structures, compound (2) is present as two conformers, with small differences in the spatial arrangement of the cyclo-octadiene rings. Both of them present a transoid conformation of the aromatic rings, with a dihedral angle of 118°. In contrast, (3) is in cisoid form, while (4) presents an almost perpendicular geometry, the angle between the phenyl groups being 66° and 93°, respectively. We have taken these structures for our calculations; in particular, the geometry of the conformer denoted as (A) in ref. [7] has been used for the derivative (2). The structure of compound (1) has been obtained from that of molecule (2), by replacing a methylene with a carbonyl group, and then optimizing the geometry by a molecular mechanics calculation based on mm+ force field [9].

It is worth remembering that, if the enantiomer with R absolute configuration is considered, the structures described so far correspond to P helicities of the biphenyl skeleton for the compounds (1), (2), and (4), while the helicity is M for derivative (3).



(1) (2) (3) (4)

β/μm^{-1} +58 +19.8 -21 +2.0

FIGURE 1. Biphenyl derivatives and corresponding helical twisting power measured in the liquid crystal mixture E7 [6].

The experimental twisting power values can be compared with the calculated chirality order parameters, whose behaviour is shown in Fig. 2 for a range of ε values corresponding to reduced temperatures reasonable for liquid crystal phases.

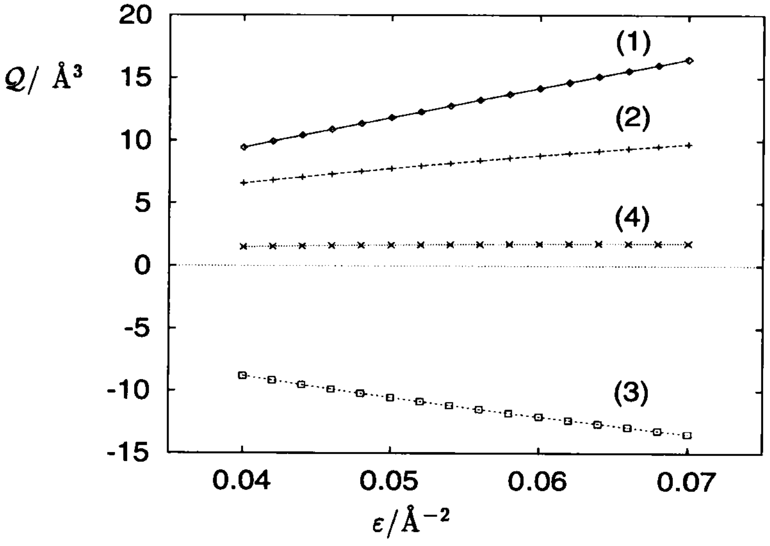


FIGURE 2. Chirality order parameter Q as a function of ε.

We see from the figure that the trend of the chirality order parameters parallels that of the experimental twisting powers, and the signs are correctly predicted. At around room temperature, corresponding to $\varepsilon \approx 0.05\text{Å}^{-2}$, the factor relating theoretical chirality order parameters and measured twisting power data comes out to be of the order of the unity, in agreement with the value of $\varepsilon/2\pi K_{22}v_m$ computed for E7. At present, it is not the case to go into more detailed comparisons, since the calculations have been performed on the basis of approximate molecular structures. We have seen that in general the numerical results are rather insensitive to slight changes in the geometries, such as those bringing conformer A into conformer B in the case of molecule (2). However it has to be remarked that the geometries of the molecules dissolved in liquid crystals might be well different from those obtained from X-ray. In addition, in our calculations the molecular flexibility has been completely disregarded. In particular, for the open derivative (4) a single conformer has been considered, while the torsional angle distribution should be taken into account.

The results can be explained by considering in detail surface tensor (or equivalently ordering matrix) and helicity tensor for each of the four molecules. They are reported in Table 1, where a, b, c denote the principal axes of the $\underline{\underline{Q}}$ tensor, and x, y, z those of the surface tensor. We have labelled as z and y the axes with highest and lowest tendency to align with the director, respectively. In all cases the y direction is close to that of the line bisecting the obtuse angle between phenyl ring planes.

We see from the Table that the principal values of both surface and helicity tensor are not very different for compounds (1) and (2), and this is not surprising given the close similarity of the two molecules. As shown by the values of order parameters, they have a disc-like behaviour, with a rather strong tendency to maintain the y axis perpendicular to the mesophase director. However, while in (2) all directions in the xz plane are almost equivalent, in (1) the presence of carbonyl groups has the effect of introducing an axis of preferential alignment, approximately perpendicular to the phenyl-phenyl bond. It follows that the principal axes of the surface tensor are very close to those of the helicity tensor.

Going from derivatives (1) and (2) to (3), small effects on the components of the surface tensor, and therefore on the orientational behaviour, are predicted, while the helicity tensor components change their signs, so that a negative Q value is obtained.

A completely different behaviour is predicted for the unique member of the group possessing an open structure. The orienting behaviour of the molecule, for which an almost perpendicular arrangement of the phenyl rings is assumed [7], is rod-like. From the point of view of the chiral properties the compound, in agreement with the simple model of two identical planar moieties connected by a bond [3], is characterized by a very low helicity along the axis parallel to that bond, and much higher helicities, almost equal in magnitude and opposite in sign, along axes bisecting the dihedral angles between the phenyl rings. The predicted twisting power is, in agreement with experiment, smaller than that of all other molecules of the series.

TABLE 1. Principal elements of the surface tensor, diagonal elements of the helicity tensor in the principal axis system of the surface tensor and in its principal frame, and principal values of the ordering matrix, calculated with $\varepsilon = 0.05$ Å^{-2}.

compound	(1)	(2)	(3)	(4)
Ph-Ph bond	$\sim\parallel$ x axis	on xz plane	$\sim\parallel$ x axis	$\sim\parallel$ z axis
$T_{xx}/\mathrm{\AA}^2$	7.6	12.8	10.8	-8.1
$T_{yy}/\mathrm{\AA}^2$	-26.1	-27.8	-23.8	-12.1
$T_{zz}/\mathrm{\AA}^2$	18.5	15.0	13.0	20.2
$Q_{xx}/\mathrm{\AA}^3$	45.5	19.2	-38.2	-71.6
$Q_{yy}/\mathrm{\AA}^3$	14.1	22.5	-33.4	71.2
$Q_{zz}/\mathrm{\AA}^3$	-59.6	-41.7	71.6	0.4
$Q_{aa}/\mathrm{\AA}^3$	45.8	41.2	-68.7	-71.9
$Q_{bb}/\mathrm{\AA}^3$	14.1	21.4	-2.9	71.3
$Q_{cc}/\mathrm{\AA}^3$	-59.9	-62.6	71.6	0.6
S_{xx}	0.031	0.106	0.095	-0.122
S_{yy}	-0.241	-0.249	-0.224	-0.152
S_{zz}	0.210	0.143	0.129	0.274

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APPENDIX

Home-made programs for the numerical evaluation of the helical twisting power are used in connection with other software packages necessary to obtain molecular structures or to analyse and visualize data. A graphical interface based on a menu system has been created to manage the various programs and to generate compatible input/output files. The interface (a script-file using the free-library TCL/TK) and its components have been created for a DEC 3000/500 Alpha processor, with operating system OSF/1 3.2c; they can however be easily adapted to other systems. Source codes and binary files are freely available at the anonymous site cfalfa.chfi.unipd.it:/pub/software/htp (147.162.53.5:/pub/software/htp).

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